

New Direct Iodination of Tetrathiafulvalene (TTF): Mono- and Di-iodo-TTF and their X-Ray Crystal Structures

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2-Iodo- (**1**) and 2,6(7)-diiodo-tetrathiafulvalenes (**2a**, **2b**) have been synthesized in good yields, by treating the corresponding lithiated intermediates of TTF with perfluorohexyl iodide; the X-ray crystal structures of **1** and **2a** have been determined.

Halogenated TTF derivatives, especially iodinated ones, are potentially important compounds as intermediates for further TTF derivatization, as well as for their intrinsic value as donors with an increased tendency to participate in intermolecular interactions compared to TTF, in charge transfer (CT) complexes and ion-radical salts.^{1,2} The present communication describes a new route for mono- and di-iodination of the corresponding lithiated TTF derivatives, and the X-ray crystal structures of two of the resulting iodinated products.

To date, there have been very few reports of methods for preparing halogenated TTF derivatives,¹⁻⁵ and among these the X-ray crystal structure of only 2,3-dibromo-TTF has been determined.⁴ Moreover, there is still some uncertainty about the nature of products and the convenience of the synthesis of iodinated TTF derivatives. The first attempt at iodination of TTF was made by Kreicberga *et al.*⁵ They used a rather formidable procedure, starting from 2,6(7)-dibutoxycarbonyl-TTF via Grignard intermediates and subsequent hydrolysis and decarboxylation, affording presumably 2-iodo-TTF **1** (mp 66–68 °C) and 2,6(7)-diiodo-TTF **2** in 9 and 16% yields, respectively. Recently, a direct iodination method based on the reaction of lithiated TTF and tosyl iodide was reported.¹ However, a contradictory melting point (110–112 °C) for **1** with the above value was reported, which indicates that **1** was not obtained in both cases, although the authors of ref. 1 claimed that both the ¹H NMR and CV data were consistent with formula **1**.

The work reported here utilizes perfluorohexyl iodide (PFHI) as an iodinating agent for lithiated TTF intermediates, to obtain both **1** and **2** in good yields (≈70%). In a typical experiment for the preparation of **1**, PFHI (1.5 equiv.) was added to a lithiated TTF solution in THF, prepared earlier from TTF (1 equiv.) and lithium diisopropylamide (LDA, 1.5 equiv.), at –60 °C. The reaction mixture was stirred at low- (1 h) and room-temperature (1 h) and was then quenched with water and extracted into diethyl ether. Purification by silica-gel column chromatography [1:1 mixture of CS₂ and light petroleum (bp 40–60 °C) as eluent] and then crystallization from light petroleum resulted in the formation of orange needles with mp 68.8–69.3 °C, similar to that reported in ref. 5. Its structure was confirmed by ¹H and ¹³C NMR† spectroscopy and by X-ray diffraction.‡

Similarly, a mixture of isomers of **2** was obtained in ≈72% yield, by using TTF (1 equiv.), LDA (4 equiv.) and PFHI (4 equiv.). Slow evaporation of the solution (CS₂–light petroleum, 1:1) yielded two kinds of crystals: orange-red needles (mp 122.4–122.7 °C) and orange plates (mp 100.0 °C, decomp. ca. 130 °C). The plates proved to be 2,6-diiodo-TTF, as determined by X-ray diffraction analysis.‡ The ¹H and ¹³C NMR of this mixture were also determined.† Coincidentally, both isomers afford identical chemical shifts (within experimental error), as found earlier for other 2,6(7) disubstituted TTF derivatives.⁶

The crystal structures of **1** and **2a** are shown in Fig. 1. Both are characterized by plane-to-plane stacking of the molecules.



Apparently, there is a marked difference in the stereochemical preferences of the positional dihalogenation of TTF for dichloro-TTF **3**,¹ dibromo-TTF **4**⁴ and diiodo-TTF. In the former two cases, dihalogenation takes place generally at the 2 and 3 positions. In the latter, however, diiodination occurs primarily at the 2 and 6(7) positions. The facile formation of **3** and **4** is attributed to the activating effect of the first bromine or chlorine atom which is introduced onto the TTF moiety.⁷ The formation of **2** (rather than the corresponding diiodo isomer analogue of **3** and **4**) may result from the steric

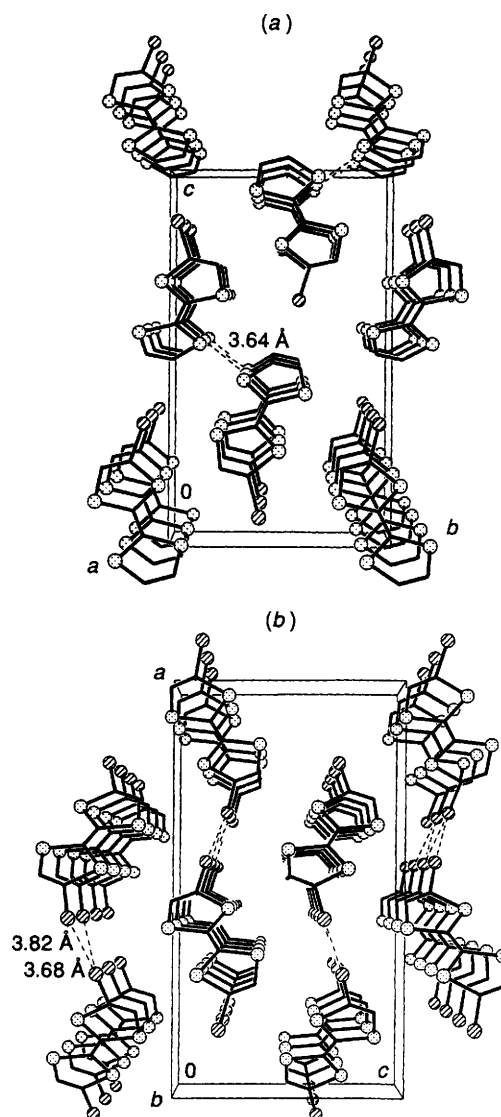


Fig. 1 (a) Packing diagram of 2-iodo-TTF **1** viewed down the crystallographic *a* axis. The only intermolecular distance less than the sum of the van der Waals radii (S...S) is shown. (b) Packing diagram of 2,6-diiodo-TTF **2a** viewed down the crystallographic *b* axis. The two I...I distances less than the sum of the van der Waals radii are shown. There are no S...S distances less than the sum of the van der Waals radii.

hindrance exerted by the two neighbouring iodine atoms. This effect also explains why tri- and tetra-iodo-TTF derivatives have not yet been prepared, although the corresponding bromo and chloro derivatives are rather easily obtained.[§]

Cyclic voltammetric data for both **1** and **2** are listed in Table 1. Like other TTF derivatives, both compounds display two characteristic reversible one-electron oxidation waves. However, the introduction of iodine atoms on the TTF moiety shifted the oxidation potentials anodically, even though the electronegativity of iodine is similar to that of carbon. This phenomenon is in accordance with previous reports.^{1,8} In comparison with TTF, both **1** and **2** exhibit a unique irreversible reduction wave at about -1.5 V, in benzonitrile. Subsequent oxidation of **2** after its reduction results in a new pair of reversible oxidation waves at 0.50 and 0.91 V, in addition to the original one. Compound **1** presents similar electrochemical behaviour to **2**, but the two pairs of oxidation waves are nearly overlapped and both the new and original peaks exhibit similar oxidation potentials (Table 1). The reduction waves exhibited by the iodo-TTF derivatives are attributed to the cathodic cleavage of the carbon-iodine bond, leading to the formation of TTF, as has been demonstrated by electrolysis.

We have also found that deiodination of **1** and **2** can be easily achieved by reduction with sodium borohydride. Thus, 1 equiv. of a 0.1 mol dm⁻³ solution of sodium borohydride in *N*-methylpyrrolidone or hexamethylphosphoric triamide was added dropwise, at room temperature, to a stirred solution containing 1 equiv. of **2**. The reaction mixture was then heated to 40 °C for 0.5 h until evolution of gas ceased, resulting in the formation of a mixture of TTF, **1** and unreacted **2**. Addition of 1 more equiv. of sodium borohydride to the mixture, followed by stirring for 4 h at room temperature, yielded TTF exclusively. Attempts to reduce chloro-TTF derivatives under similar conditions have been unsuccessful. However, the four bromine atoms in tetrabromo-TTF^{||} could be removed in a stepwise manner, during the addition of 1–4 equiv. of sodium borohydride, consecutively. This dehalogenation process could provide a useful and flexible positional protective

strategy for TTF derivatizations, which is being examined in our laboratory.

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Footnotes

† **1**, NMR (CDCl₃, TMS): ¹H δ, 6.33(s, 2H), 6.42(s, 1H); ¹³C, δ 63.76, 124.41, 119.09, 111.17, 112.96. **2a, b**, NMR (CDCl₃, TMS): δ 6.42(s); ¹³C, δ 63.59, 124.22, 113.77.

‡ Reflections were measured at room temperature with Syntex P1 diffractometer [$\lambda(\text{Mo-K}\alpha) = 0.71069$ Å, graphite monochromator, $\omega/2\theta$ scan]. The structures were solved by direct methods with full-matrix least-squares refinement and anisotropic displacement parameters for non-hydrogen atoms. All calculations were carried out using SHELX76 and SHELX86 programs.

Crystal Data for **1**: C₆H₃IS₄, $M = 330.2$, orthorhombic, $P2_12_12_1$, $a = 5.044(2)$, $b = 10.795(2)$, $c = 17.872(4)$ Å; $V = 973.1(5)$ Å³, $Z = 4$, $D_c = 2.254$ Mg m⁻³, $\mu = 4.081$ mm⁻¹, $F(000) = 624$, $R = 0.0338$, $R_w = 0.0345$, GOF = 1.55 for 898 observed reflections [$F > 4\sigma(F)$] out of 1193 independent ones measured ($2 < 2\theta < 54^\circ$).

Crystal Data for **2**: C₆H₃I₂S₄, $M = 456.1$, orthorhombic, $Pna2_1$, $a = 19.100(4)$, $b = 5.375(2)$, $c = 10.899(2)$ Å; $V = 1118.9(6)$ Å³, $Z = 4$, $D_c = 2.708$ Mg m⁻³, $\mu = 6.313$ mm⁻¹, $F(000) = 832$, $R = 0.0404$, $R_w = 0.0423$, GOF = 1.26 for 773 observed reflections [$F > 4\sigma(F)$] out of 1037 independent ones measured ($2 < 2\theta < 52^\circ$).

We note that **1** crystallizes in a chiral space group, and **2** in a polar one, in crystal classes 222 and *mm2* respectively. Both crystal classes give a non-zero piezoelectric tensor, which means they can exhibit second harmonic generation (SHG). None was found on powder samples of the two compounds. 1,2-Dibromo-TTF⁴ crystallizes in the chiral polar space group, $P2_1$, indicating that there may be a preference for TTF derivatives to crystallize in non-centrosymmetric space groups. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ When LDA (5 equiv.) or *n*-butyllithium were used to lithiate TTF (1 equiv.), followed by a reaction with an excess of PFHI, no tri- or tetra-iodo-TTF derivatives could be isolated. Under similar conditions, tetrachloro- and tetrabromo-TTF were formed easily.

|| This compound was described by the authors of ref. 2, who obtained it in 14% yield. Our procedure, which has improved the yield to 40%, will be published elsewhere.

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Table 1 Peak potentials of iodo-TTF derivatives^a

Compd.	E_p^{red}	E_{p1}^{ox}	E_{p2}^{ox}	E_{p3}^{ox}	E_{p4}^{ox}
TTF		0.53	0.93		
1	-1.53	0.60	1.00		
1^b		0.49	0.60	1.00	
2	-1.53	0.69	1.05		
2^b		0.50	0.69	0.91	1.05

^a In V relative to Ag/AgCl reference electrode in benzonitrile-0.1 mol dm⁻³ tetrabutylammonium tetrafluoroborate, on glassy carbon working electrode, sweep rate: 100 mV s⁻¹. ^b Subsequent oxidation sweep after the reduction down to -2.00 V.